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TURUN PAT.TSTO

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## DECLARATION

I, the undersigned, hereby certify that to the best of my knowledge and belief the following is a true translation of the Finnish patent application No. 973427.

Declared at Turku, February 28, 2001.



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F1000103051B



SUOMI-FINLAND  
(FI)

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Patent- och registerstyrelsen

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(72) Keksijä - Uppfinnare

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(74) Asiamies - Ombud: Turun Patenttitoimisto Oy, PL 99, 20521 Turku

(54) Keksinnön nimitys - Uppfinningens benämning

Uusia blokkikopolyymeerejä ja niiden valmistus  
Nya block-kopolymerer och deras framställning

(56) Viitejulkaisut - Anförda publikationer

Makromol. Chem. 185 (1984), p. 2625-2645,  
Makromol. Chem. 186 (1985), p. 357-366

(57) Tiivistelmä - Sammandrag

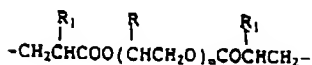
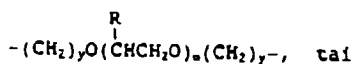
Keksinnön kohteena on uusi polysilok-  
saanipohjainen blokkikopolymeeri, jonka  
kaava on

$T(AB)_nAT$  (I)

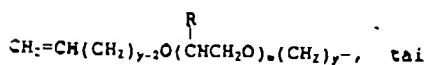
jossa

$A = -(SiR'R''O)_nSiR'R''-$ , jossa  $R'$  ja  $R''$   
ovat samoja tai erilaisia ja ovat alempi  
alkyyli- tai fenyyli- tai fenyyli- tai fenyyli-  
nitti alkyyli- tai fenyyli- tai fenyyli-  
substituoitu tai substituimaton,  
B on polyalkyleenioksidi, jonka kaava on

jossa R on vety, alempi alkyyli tai fenyy-  
li;  $R_1$  on vety tai alempi alkyyli; y on  
2...6; m on 3...30; n on 5...3000; ja x on  
0...100.

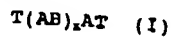


ja T on



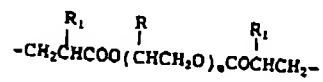
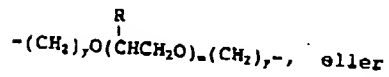
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Uppfinningen gäller en ny  
polysiloxanbaserad block-kopolymer, vars  
formel är

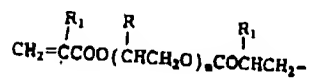
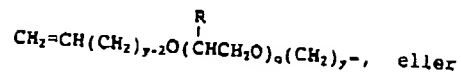


där

A = -(SiR'R''O)<sub>n</sub>SiR'R''-, där R' och R'' är  
samma eller olika och är en lägre alkyl-  
eller fenylgrupp, varvid nämnda alkyl-  
eller fenylgrupp kan vara substituerad  
eller osubstituerad,  
B är en polyalkylenoxid, vars formel är



och T är



där R är väte, lägre alkyl eller fenyl; R<sub>1</sub>  
är väte eller lägre alkyl; y är 2...6; n är  
3...30; n är 5...3000; och x är 0...100.

## NEW BLOCK COPOLYMERS AND PREPARATION THEREOF

The invention relates to new polysiloxane based block copolymers and to the preparation thereof.

Silicones, or polyorganosiloxanes, represent a broad spectrum of synthetic silicon based polymers of formula  
5 (R'R''SiO)<sub>n</sub>, where R' and R'' represent alkyl groups, usually methyl, ethyl, propyl, or phenyl groups. In the literature, various methods for the preparation of siloxanes are known, for example, Walter Noll, Chemistry and Technology of Silicones, Academic Press, Orlando, 1968,  
10 190-245, and John C Saam, in John M Zeigler and F W Gordon Fearon, ed., Silicon-Based Polymer Science, A Comprehensive Resource, Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1990, 71-90.

Polysiloxanes, particularly poly(dimethyl siloxanes), are  
15 used extensively as such in technical applications.

Copolymers of polysiloxane and poly(alkylene oxide) are known. Known copolymers of this type are useful as emulsifiers and stabilizers. The preparation of such copolymers by hydrosilylation has been reported in the  
20 literature (Polysiloxane Copolymers/Anionic Polymerization, Springer-Verlag Berlin Heidelberg 1988, pp. 46-47; H W Haesslin & H F Eicke, Makromol Chem 185, 2625-2645, (1984); H W Haesslin, Makromol Chem 186, 357-366 (1985), and M Galin & A Mathis, Macromolecules 1981, 14, 677-683. The  
25 preparation of block copolymers AB, ABA and (AB)<sub>n</sub>, where A represents poly(ethylene oxide) (PEO) and B is poly(dimethyl siloxane), by hydrosilylation of mono- or diallyl-terminated PEO-oligomers and Si-H-terminated PDMS oligomers with hexachloroplatinic acid as a catalyst, was  
30 reported by Haesslin. The molecular weight of PDMS-oligomer was 1000 g/mol and the molecular weight of ternary block copolymers (ABA) was between 1550 g/mol and 1800 g/mol.

Haesslin & Eike describe ternary block copolymers PEO-PDMS-PEO, where the molecular weight of PDMS is 1000 g/mol and the molecular weight of PEO-block is between 100 g/mol and 750 g/mol.

- 5 Galin & Mathis describe the preparation of ternary PDMS-PEO-PDMS block copolymers. The molecular weight of PDMS was between 1000 g/mol and 4700 g/mol and the molecular weight of PEO was between 6200 g/mol and 10,700 g/mol.

- European Patent Publication EP 545,002 describes grafted  
10 polysiloxanes prepared by hydrosilylation of polysiloxanes with polyalkylene oxides of formula  $\text{CH}_2=\text{CHCH}_2\text{O}(\text{CHRCH}_2\text{O})_n\text{CH}_2\text{CH}=\text{CH}_2$ . In these polymers, the polyether moieties are linked to the alkyl substituent of silicon instead of being linked to the stem.

15 OBJECT OF THE INVENTION

- This invention is directed to providing new alkylene terminated polysiloxane-poly(alkylene oxide)-based block copolymers of controlled polarity for the preparation of elastomers, either as such or as a component in the  
20 elastomeric structure or as a component in the mixture of an elastomeric composition. The new copolymers must satisfy the following criteria:

1. In the preparation of elastomers, the copolymer should be capable of crosslinking, for example by hydrosilylation.  
25 Thus the copolymer should include an alkyl-terminated polyalkylene oxide block at both of its ends to allow crosslinking by hydrosilylation. The copolymers described in Galin & Mathis do not satisfy this condition.
2. The molecular weight should be at least 20,000 g/mol,  
30 preferably from about 40,000 g/mol to about 300,000 g/mol. The ternary block copolymers described in Haesslin & Eicke are markedly smaller. Moreover, it is of importance that

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polysiloxane and polyalkylene oxide blocks are linked to each other by silicon-carbon bonds.

3. The copolymer must exist in one phase. If the molecular weight of the polyalkylene block is too high in relation to the molecular weight of the polysiloxane unit, phase separation will occur.

#### SUMMARY OF THE INVENTION

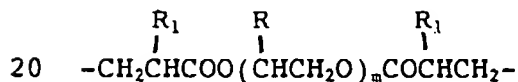
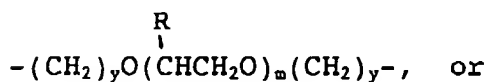
Thus, the invention is directed to a new polysiloxane-based block copolymer of formula



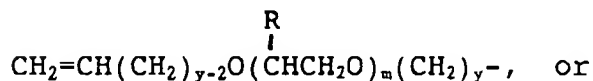
wherein

- A =  $-(SiR'R''O)_nSiR'R''-$ , wherein R' and R'' are the same or different and represent a lower alkyl group or a phenyl group, where said alkyl or phenyl group may be substituted or unsubstituted;

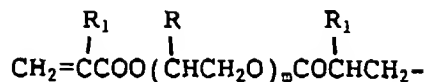
B is polyalkylene oxide of formula



and T is



4



wherein

R is hydrogen, lower alkyl, or phenyl,

5 R<sub>1</sub> is hydrogen or lower alkyl,

y is 2 - 6,

m is 3 - 30,

n is 5 - 3000, and

x is 0 - 100.

10 The term "lower alkyl" represents C<sub>1</sub>-C<sub>6</sub> alkyl groups.

The substituents R' and R'' of formula (I) are preferably both methyl groups.

The number y is preferably 2.

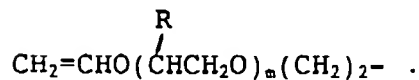
R is preferably hydrogen, methyl, or phenyl.

15 According to a preferred embodiment, the B in the formula (I) is

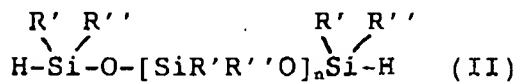


and T is

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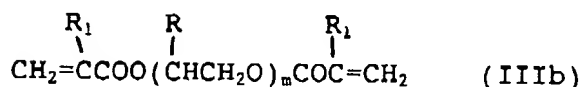
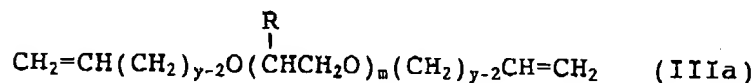


The invention is also directed to a method for the preparation of new compounds of formula (I). The method is  
 25 characterized in that the polysiloxane of formula (II)



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wherein R' and R'' are the same, or different, lower alkyl or phenyl groups, where said alkyl or phenyl group may be substituted or unsubstituted, is reacted, in the presence of a catalyst, with a polyalkylene oxide of formula (IIIa) or (IIIb)



10 where R, R<sub>1</sub>, n, and m are the same as above.

Preferred compounds of the group IIIa include vinyl or allyl terminated polyethylene glycol. A preferred compound of the group IIIb is, for example, methacryl terminated polyethylene glycol.

- 15 A preferred catalyst is a noble metal catalyst, most generally a platinum complex in alcohol, xylene, divinyl siloxane, or cyclic divinyl siloxane. An especially preferred catalyst is Pt(0)divinyl tetramethyl siloxane complex.
- 20 In order to prepare the  $\alpha,\omega$ -alkylene terminated PEO(PDMS-PEO)<sub>n</sub> copolymer, the compound of formula (IIIa) or (IIIb) must be used in excess in relation to the compound of formula (II). Preferably, the molar ratio

$$\frac{\text{compound of formula (IIIa) or (IIIb)}}{\text{compound of formula (II)}}$$

is between 1.05 and 2.0.



The invention is disclosed below in greater detail with reference to the examples.

#### EXAMPLE 1

Procedure for an  $\alpha,\omega$ -vinyl terminated PEO-(PDMS-PEO)<sub>n</sub> polymer, where the hydride terminated PDMS has a molecular weight of 5000 g/mol and the vinyl terminated PEO has a molecular weight of 240 g/mol.

0.528 g of anhydrous vinyl-terminated polyethylene glycol (PEOVI,  $\alpha,\omega$ -vinyl-terminated) with a molecular weight of 240 g/mol is weighed to a dried three-necked flask with a capacity of 50-100 ml. In addition, to the same vessel is added 10 g of polydimethyl siloxane (PDMS,  $\alpha,\omega$ -hydride-terminated,  $M_n = 5000$  g/mol). The content of hydride groups in PDMS is 0.04 % by weight resulting in 4 mmol of hydride groups per 10 grams with the amount of previously weighed PEOVI-vinyl groups being 4.4 mmol ( $= 2 \times 0.528/240$  mol). The excess of the vinyl groups in the reaction results in vinyl groups in both ends of the final product, which is a prerequisite for the subsequent crosslinking. In addition, toluene, dried by distillation, is added to the reaction such that its content is 30 % (4.5 g) by weight, in order to facilitate mixing and to keep the reaction from occurring too vigorously. The reaction solution is stirred over a magnetic stirring plate at 400 rpm and dry oxygen is bubbled through the solution (about three bubbles per second), which prevents the conversion of the catalyst to a metallic state, thus preventing the deactivation of the catalyst. After addition of the catalyst (Pt(0)divinyl tetramethyl siloxane complex) through the septum, the reaction solution is warmed to 50 °C. The amount of the catalyst is 50 ppm based on the total amount of reactants participating in the reaction. The catalyst is added dropwise thus preventing the formation of hot spots in the reactor. Upon addition of the catalyst the polymerization is allowed to proceed for 2 hours. The completion of the

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reaction is then confirmed by IR (the loss of Si-H-peak at  $2130\text{ cm}^{-1}$ ). Upon the cessation of the polymerization the reaction is warmed to  $65\text{ }^{\circ}\text{C}$  and toluene removed under vacuum (4 mm Hg) for 30 minutes. The absence of toluene is  
5 detected most preferably by using NMR.

#### EXAMPLE 2

Procedure for  $\alpha,\omega$ -allyl-terminated PEO-(PDMS-PEO)<sub>n</sub> polymer where PDMS has a molecular weight of 5000 g/mol and the allyl terminated PEO has a molecular weight of 520 g/mol:

- 10 To a dried three-necked flask with a capacity of 50-100 ml is weighed anhydrous allyl-terminated polyethylene glycol (PEOA,  $\alpha,\omega$ -allyl-terminated) having a molecular weight of 520 g/mol, and hydride-terminated polydimethyl siloxane (PDMS,  $\alpha,\omega$ -hydride terminated  $M_n = 5000\text{ g/mol}$ ). The mass of  
15 PEOA is 1.38 g (5.28 mmol of allyl groups) and the mass of PDMS is 12 g (4.8 mmol of hydride groups), and thus the amount of allyl groups exceeds the amount of the hydride groups by 10 per cent. This secures an allyl terminated end product. In addition, toluene is weighed to the reaction  
20 vessel such that it represents 45 % (7.2 g) by weight. The reaction mixture is stirred on a magnetic stirring plate at 400 rpm and dry oxygen is bubbled through the mixture (about three bubbles per second). The reaction mixture is brought to a temperature of  $60\text{ }^{\circ}\text{C}$ . The catalyst  
25 (Pt(0)divinyl tetramethyl siloxane complex) is then cautiously added to the mixture through the septum one drop at a time. The amount of the catalyst is 50 ppm based on the added reactants. The polymerization is allowed to proceed for 6 hours and the completion of the  
30 polymerization is then confirmed by IR (the loss of the Si-H-peak at  $2130\text{ cm}^{-1}$ ). For the removal of toluene the reaction is brought to  $65\text{ }^{\circ}\text{C}$  and toluene removed under vacuum (4 mm Hg) for 30 minutes. The absence of toluene is detected by NMR.

EXAMPLE 3

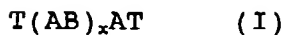
Procedure for monophasic  $\alpha,\omega$ -methacryl terminated PEO-  
(PDMS-PEO)<sub>n</sub> polymer, where the hydride-terminated PDMS has a  
molecular weight of 5000 g/mol and the methacrylated PEO  
5 has a molecular weight of 538 g/mol

To a dried three-necked flask with a capacity of 50-100 ml  
is weighed anhydrous methacryl-terminated polyethylene  
glycol (PEOMA,  $\alpha,\omega$ -methacryl-terminated) with a molecular  
weight of 538 g/mol, and hydride-terminated polydimethyl  
10 siloxane (PDMS,  $\alpha,\omega$ -hydride terminated  $M_n = 5000$  g/mol). The  
mass of PEOMA is 1.184 g (4.4 mmol of methacryl groups) and  
the mass of PDMS is 10 g (4.0 mmol of hydride groups), and  
thus the amount of methacryl groups exceeds the amount of  
the hydride groups by 10 per cent. This secures a methacryl  
15 terminated end product. In addition, toluene is weighed to  
the reaction vessel such that it represents 45 % (9.2 g) by  
weight. The reaction mixture is stirred on a magnetic  
stirring plate at 400 rpm and dry oxygen is bubbled through  
the mixture (about three bubbles per second). The reaction  
20 mixture is brought to a temperature of 60 °C. The catalyst  
(Pt(0)divinyldimethyl siloxane complex) is then added to  
the mixture through the septum one drop at a time. The  
amount of the catalyst is 50 ppm based on the added  
reactants. The polymerization is allowed to proceed for  
25 20 hr and the completion of the polymerization is then  
confirmed by IR (the loss of the Si-H-peak at 2130  $\text{cm}^{-1}$ ).  
For the removal of toluene the reaction is brought to 65 °C  
and toluene removed under vacuum (4 mm Hg) for 30 minutes.  
The absence of toluene is detected by using NMR.

30 For an expert in the art it is clear that the different  
embodiments of the invention may vary within the scope of  
the claims presented below.

# CLAIMS

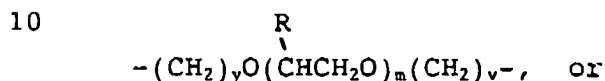
1. A new polysiloxane-based block copolymer characterized by the formula



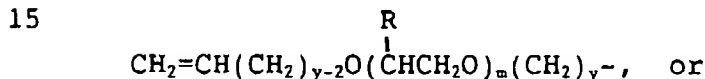
wherein

5 A =  $-(SiR'R''O)_nSiR'R''-$ , wherein R' and R'' are the the same or different and represent a lower alkyl group or a phenyl group, where said alkyl or phenyl group may be substituted or unsubstituted;

B is polyalkylene oxide of formula



and T is



wherein

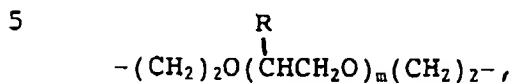
20 R is hydrogen, lower alkyl, or phenyl; R<sub>1</sub> is hydrogen or lower alkyl; y is 2 - 6; m is 3 - 30; n is 5 - 3000; and x is 0 - 100.

2. The block copolymer according to claim 1, characterized

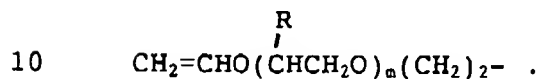
10

in that R' and R'' in the formula (I) are each methyl groups; y is 2; and R is hydrogen, methyl, or phenyl.

3. The block copolymer according to claim 1 or 2, characterized in that B in the formula (I) is



and T is

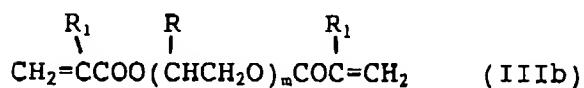
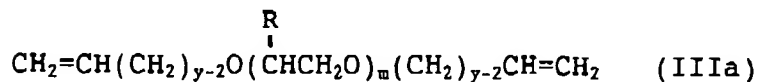


4. A method for the preparation of a polysiloxane-based block copolymer (I) of claim 1, characterized in that a polysiloxane of formula (II)



wherein R' and R'' are the same or different and represent a lower alkyl group or a phenyl group, where said alkyl or phenyl group may be substituted or unsubstituted;

20 is reacted in the presence of a catalyst with a polyalkylene oxide of formula (IIIa) or (IIIb)



25 wherein R, R<sub>1</sub>, n, and m are the same as defined in claim 1.

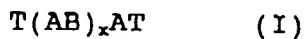
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5. The method according to claim 4, characterized in that the catalyst is a noble metal catalyst, such as a platinum complex in alcohol, xylene, divinyl siloxane, or cyclic vinyl siloxane.
- 5 6. The method according to claim 5, characterized in that the catalyst is a Pt(0)divinyl tetramethyl siloxane complex.

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# ABSTRACT

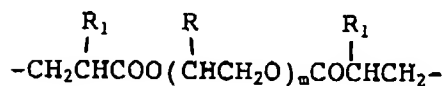
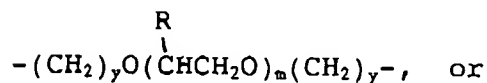
The invention relates to a new polysiloxane-based block copolymer having a formula



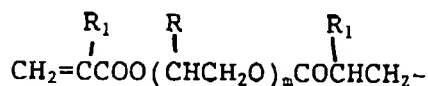
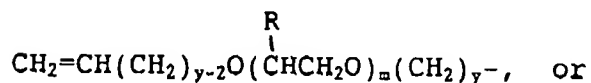
wherein

A =  $-(SiR'R''O)_nSiR'R''-$ , wherein R' and R'' are the the same or different and represent a lower alkyl group or a phenyl group, wherein said alkyl or phenyl group may be substituted or unsubstituted;

B is polyalkylene oxide of formula



and T is



wherein

R is hydrogen, lower alkyl, or phenyl; R<sub>1</sub> is hydrogen or lower alkyl; y is 2 - 6; m is 3 - 30; n is 5 - 3000; and x is 0 - 100.

**PATENTTI- JA REKISTERIHALLITUS**

**TUTKIMUSRAPORTTI**

Patentti- ja innovaatiolinja

<b>PATENTTIHAKEMUS NRO</b>	<b>LUOKITUS</b>
981506	C08G 77/46, A61K 9/58, 31/56

**TUTKITTU AINEISTO**

Patenttijulkaisukokoelma (FI, SE, NO, DK) tutkitut luokat

C08G 77/46, A61K 9/52-58, 31/56-585

**Tiedonhaut ja muu aineisto**

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EPO documentation, EPO, World Patents Index, Derwent, Patent Abstracts of Japan, JPO. 1970- [online] EPOQUE

**VIITEJULKAISUT**

Kategoria <sup>1)</sup>	Julkaisun tunnistetiedot	Koskee vaatimuksia
X	EP A1 545002, C08G 77/46	1-22
Ks. välipäätös	EP A1 882753, C08G 77/38	1-22
Ks. välipäätös	FI-A0 973427, C08G 77/46	1-22
X	J. Of Controlled Release, 10 (1989), Katherine L. Ulman & al. "Drug permeability of modified silicone polymers. I. Silicone- organic block copolymers", s. 251-260	1-22
X	Chemical Abstracts [CD-ROM]. American Chemical Society. Tiivistelmä 126:200090 Synthesis and drug release property of polysiloxane containing pendant long alkyl ether group. Hu, Yunhua; Zhuo, Renxi (Department Chemistry, Wuhan University, Wuhan 430072, Peop. Rep. China). Gaofenzi Xuebao, (1), 62-67 (Chinese) 1997 Kexue	1-22

- \*) X Patentoitavuuden kannalta merkittävä julkaisu yksinään tarkasteltuna  
Y Patentoitavuuden kannalta merkittävä julkaisu, kun otetaan huomioon tämä ja yksi tai useampi samaan kategoriaan kuuluva julkaisu  
A Yleistä tekniikan tasoa edustava julkaisu, ei kuitenkaan patentoitavuuden este

<b>Päiväys</b> 8.2.1999	<b>Tutkija</b> Liisa Helle
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Translation of the Search Report of the patent application FI 981506

Board of Patents and Registrations  
Section of patents and innovations

Search Report

Patent application no.  
981506

International Classification  
C08G 77/46, A61K 9/58, 31/56

Documentation searched  
Patent publication (FI, SE, NO, DK), classes searched  
C08G 77/46, A61K 9/52-58, 31/56-585

Databases and other searches  
Chemical Abstracts, American Chemical Society. 1967-[online] STN International  
EPO documentation, EPO, World Patents Index, Derwent, Patent Abstracts of Japan, JPO. 1970-[online] EPOQUE

References

Category*)	Bibliographical data	Refers to claims
X	EP A1 545002, C08G 77/46	1-22
See the Office Action	EP A1 882753, C08G 77/38	1-22
See the Office Action	FI A0 973427, C08G 77/46	1-22
X	J. of Controlled Release, 10 (1989), Katharine L. Ulman & al. "Drug permeability of modified silicone polymers. I. Silicone-organic block copolymers", p. 251-260	1-22
X	Chemical Abstracts [CD-ROM] American Chemical Society. Abstract 126:2000090, "Synthesis and drug release property of polysiloxane containing pendant long alkyl ether group". Hu, Yunhua; Zhuo, Renxi (Department Chemistry, Wuhan University, Wuhan 430072, Peop. Rep. China). Gaofenzi Xuebao, (1), 62-67 (Chinese) 1997 Kexue	1-22

\*)

X a relevant document concerning the patentability when taken alone

Y a relevant document concerning the patentability when taken together with one or more of the documents in the same category

A a document representing the general state of the art, not a bar to patentability

Date 8.2.1999

Examiner Liisa Helle